New mean field theories for the liquid-vapor transition
of charged hard spheres.

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The phase behavior of the primitive model of electrolytes is studied in the framework of various mean field approximations obtained recently by means of methods pertaining to statistical field theory (CAILLOL, J.-M., 2004, *J. Stat. Phys.*, **115**, 1461). The role of the regularization of the Coulomb potential at short distances is discussed in details and the link with more traditional approximations of the theory of liquids is discussed. The values computed for the critical temperatures, chemical potentials, and densities are compared with available Monte Carlo data and other theoretical predictions.

I. INTRODUCTION

Various ionic systems including electrolyte solutions, molten salts, and colloids can be studied with a good approximation in the framework of the so-called primitive model (PM) which consists in a neutral mixture of M species of charged hard spheres (HS) of charges q_α and diameters σ_α ($\alpha = 1, \ldots, M$)[1]. Of special interest is the restricted primitive model (RPM) where $M = 2$, the spheres have all the same diameter σ, and the cations and anions bear opposite charges $\pm q$. In this paper we shall also consider the special primitive model (SPM) in which the number M of species as well as the charges q_α are arbitrary but all the ions have the same diameter σ. The case of a size assymetry of the ions will not be considered however.

We have presented elsewhere an exact field theoretical representation of the PM obtained by performing a Kac-Siegert-Stratonovich-Hubbard-Edwards (KSSHE) transformation[2,3,4,5,6,7,8] of the Boltzmann's factor[9,10,11]. Thanks to this transformation, the grand-canonical partition function (GCPF) of the PM is essentially equal to the GCPF of a fluid of bare hard spheres in the presence of an imaginary random Gaussian field $i\varphi$ (φ real) with a covariance given by the Coulomb potential. Since the action $\mathcal{H}[\varphi]$ of the KSSHE field theory can be explicitly obtained then all the sophisticated techniques developed in statistical field theory[12,13] can be applied *a priori* to the PM. Note that a KSSHE formalism can also be introduced to deal with the case of neutral fluids[14,15]; the method is thus quite general and has even been employed in numerical simulations[16]. Besides KSSHE formalism, various field-theoretic approaches have been proposed recently to study lattice and off-lattice versions of the PM. It is the place to cite the works by Di Caprio *et al.*[17,18], the phenomenological (coarse-grained) field theory of Ciach and Stell[19,20,21], and recent applications of the method of collective variables by Patsahan and Mryglod[22,23,24].

In ref. (11) we have succeeded in obtaining the free energy of the homogeneous SPM at second order loop order in the framework of KSSHE field theory. This expression is used here to construct a Landau theory[25] for the liquid-vapor (LV) transition of the model. Many mean-field (MF) like theories of the LV transition of the RPM or the SPM have been proposed and are reviewed for instance in ref. (26). The aim of building MF theories similar to those discussed in this paper is not only to attempt to reproduce more or less accurately the LV coexistence curve of the RPM and its critical point, but also to provide a good starting point for a possible renormalization group analysis of ionic criticality. An interesting step in this direction was made recently in ref. (23).

Our paper is organized as follows. In sec. II we resume and extend the analysis of ref. (11) on the KSSHE representation of the SPM. Then we specialize to the case of a binary SPM in sec. III where we give the expressions of the Landau function at the second order in the loop-expansion. This yields various MF theories for the LV transition which are studied numerically in sec. IV. We conclude in sec. V.

II. PROLEGOMENA

A. The KSSHE transform

We consider the three dimensional (3D) version of the SPM. The particles live in a domain $\Omega \subset \mathbb{R}^3$ of volume $|\Omega|$. We work in the grand canonical (GC) ensemble. Let μ_α be the chemical potential of the species α. For convenience

we shall define the dimensionless chemical potential ν_α to be $\nu_\alpha = \beta\mu_\alpha$ ($\beta = 1/kT$, k Boltzmann's constant, T temperature).

Denoting by $\boldsymbol{r}_{i_\alpha}^\alpha \in \Omega$ the position of the i_α-th ion of species α we note that only configurations $\omega \equiv (N_1; \boldsymbol{r}_1^1, \ldots, \boldsymbol{r}_{N_1}^1 | \ldots | N_\alpha; \boldsymbol{r}_1^\alpha, \ldots, \boldsymbol{r}_{N_\alpha}^\alpha | \ldots | N_M; \boldsymbol{r}_1^M, \ldots, \boldsymbol{r}_{N_M}^M)$ without overlaps of the spheres - i.e. such that $\|\boldsymbol{r}_{i_\alpha}^\alpha - \boldsymbol{r}_{i_\beta}^\beta\| \geq \sigma$ - do contribute to the GCPF $\Xi[\beta, \{\nu_\alpha\}, |\Omega|]$. It follows from this remark that the ions can be supposed to interact via a pair potential $v_{\alpha,\beta}(r) = q_\alpha q_\beta\, w(r)$ where $w(r)$ identifies of course with the Coulomb potential $1/r$ outside the HS core, i.e. for $r \geq \sigma$, but is otherwise arbitrary inside (i.e. for $r \leq \sigma$).

We have shown in previous works devoted either to neutral or charged fluids how to take advantage of the arbitrariness of $w(r)$ inside the HS core to define properly the KSSHE transform[9,10,11,14]. In the case of the SPM the crux of the whole matter is to rewrite the electrostatic part of the configurational energy as a definite positive quadratic form. Therefore the regularization of $w(r)$ for $0 \leq r \leq \sigma$ must be chosen in such a way that the Fourier transform $\widetilde{w}(k)$ is positive and $w(0)$ is finite.[8,9,10,11] Replacing the point charge q_α of each ion by a radial distribution of charges $q_\alpha \tau(r)$ smeared out inside its volume fulfills all these requirements and proves to be convenient. Thus, assuming

$$
\begin{aligned}
\tau(r) &= 0 \ \text{ if } r \geq \overline{\sigma} \equiv \sigma/2 \,, \\
\widetilde{\tau}(k) &= 1 \,,
\end{aligned}
\tag{2.1}
$$

where $\widetilde{\tau}(k)$ denotes the Fourier transform of $\tau(r)$ we indeed have

$$
\widetilde{w}(k) = \frac{4\pi\widetilde{\tau}^2(k)}{k^2} \geq 0
\tag{2.2}
$$

as required and, of course $w(r) = 1/r$ for $r \geq \sigma$ by virtue of Gauss theorem. Moreover for any reasonable distribution $\tau(r)$ the self-energy $q_\alpha^2\, w(0)/2$ of ion q_α will be a finite quantity. For instance one can chose a uniform surface distribution of charges of radius $\overline{a} = a/2 < \overline{\sigma}$, i.e.

$$
\begin{aligned}
\tau_a(r) &= \frac{1}{\pi a^2}\, \delta(\|\boldsymbol{r}\| - \overline{a}) \,, \\
\widetilde{\tau}_a(k) &= \frac{\sin k\overline{a}}{k\overline{a}} \,,
\end{aligned}
\tag{2.3}
$$

yielding the regularized $w_a(r)$

$$
\begin{aligned}
w_a(r) &= \frac{1}{r} \ \text{ for } r \geq a \,, \\
&= \frac{2a - r}{a^2} \ \text{ for } r \leq a \,.
\end{aligned}
\tag{2.4}
$$

Other types of regularization will be discussed in the remainder of the paper.

Under these hypothesis a KSSHE transform can be performed and the GCPF of the SPM can be rewritten as[11]

$$
\Xi[\{\nu_\alpha\}] = \langle \Xi_{\text{HS}}[\{\overline{\nu}_\alpha + iq_\alpha\phi\}]\rangle_{v_c} \,,
\tag{2.5}
$$

where $\overline{\nu}_\alpha = \nu_\alpha + q_\alpha^2\, w(0)/2$ is a renormalized chemical potential and $\Xi_{\text{HS}}[\{\overline{\nu}_\alpha + iq_\alpha\phi\}]$ is the GCPF of a mixture of bare hard spheres in the presence of the local chemical potentials $\overline{\nu}_\alpha + iq_\alpha\phi(\vec{r})$. The "smeared" field ϕ is defined to be the space convolution

$$
\phi(\boldsymbol{r}_1) = \beta^{1/2} \int_\Omega d^3\boldsymbol{r}_2\, \tau(\|\boldsymbol{r}_1 - \boldsymbol{r}_2\|)\varphi(\boldsymbol{r}_2)
\tag{2.6}
$$

which will be conveniently noted

$$
\phi(1) = \beta^{1/2}\, \tau(1,2)\varphi(2) \,.
\tag{2.7}
$$

Note that in the whole paper, summation over repeated indices, either discrete or continuous, will always be meant (except if explicitly stated otherwise).

The brackets $\langle\ldots\rangle_{v_c}$ in equation (2.5) denote a Gaussian average over the real scalar field $\varphi(\boldsymbol{r})$, i.e.

$$
\begin{aligned}
\langle\ldots\rangle_{v_c} &\equiv \mathcal{N}_{v_c}^{-1} \int \mathcal{D}\varphi \ldots \exp\left(-\frac{1}{2}\langle\varphi|v_c^{-1}|\varphi\rangle\right) \,, \\
\mathcal{N}_{v_c} &\equiv \int \mathcal{D}\varphi \exp\left(-\frac{1}{2}\langle\varphi|v_c^{-1}|\varphi\rangle\right) \,,
\end{aligned}
\tag{2.8}
$$

where $\mathcal{D}\varphi$ is the measure of the functional integration and

$$v_c^{-1}(1,2) = -\frac{1}{4\pi}\Delta_1\delta(1,2) \tag{2.9}$$

is the inverse of the positive operator $v_c(1,2) \equiv 1/r_{12}$. We have also made use of the convenient notation

$$\begin{aligned}\left\langle\varphi|v_c^{-1}|\varphi\right\rangle &= \int_\Omega d^3\boldsymbol{r}_1 \int_\Omega d^3\boldsymbol{r}_2 \; \varphi(\boldsymbol{r}_1) \, v_c^{-1}(\boldsymbol{r}_1,\boldsymbol{r}_2) \, \varphi(\boldsymbol{r}_2) \\ &\equiv \varphi(1)v_c^{-1}(1,2)\varphi(2) \; .\end{aligned} \tag{2.10}$$

After an integration by parts with appropriate boundary conditions one obtains the more transparent expression[8,11]

$$\left\langle\varphi|v_c^{-1}|\varphi\right\rangle = \frac{1}{4\pi}\int_\Omega d^3\boldsymbol{r} \; (\boldsymbol{\nabla}\varphi)^2 \; . \tag{2.11}$$

To make some contact with statistical field theory we finally introduce the KSSHE action or effective Hamiltonian

$$\mathcal{H}[\varphi] = \frac{1}{2}\left\langle\varphi|v_c^{-1}|\varphi\right\rangle - \ln\Xi_{\mathrm{HS}}\left[\{\overline{\nu}_\alpha + iq_\alpha\phi\}\right] \; , \tag{2.12}$$

which allows us to recast Ξ under the form

$$\Xi[\{\nu_\alpha\}] = \mathcal{N}_{v_c}^{-1}\int\mathcal{D}\varphi \; \exp(-\mathcal{H}[\varphi]) \; . \tag{2.13}$$

It is important to distinguish carefully, besides the usual GC averages $< \ldots >_{\mathrm{GC}}$, between two types of statistical field averages : the already defined $< \ldots >_{v_c}$ (cf equation (2.8)) and the $< \ldots >_{\mathcal{H}}$ defined as

$$< A[\varphi] >_{\mathcal{H}}\equiv \frac{\int\mathcal{D}\varphi \; \exp(-\mathcal{H}[\varphi])A[\varphi]}{\int\mathcal{D}\varphi \; \exp(-\mathcal{H}[\varphi])} \; . \tag{2.14}$$

Since many thermodynamic quantities of interest can be expressed in terms of the charge correlation functions $G_{\mathrm{C}}^{(n)}$[1] it is important to relate these functions to the field correlation functions $G_\varphi^{(n)}$. More precisely one has

$$\begin{aligned}G_{\mathrm{C}}^{(n)}(1,\ldots,n) &= \; <\widehat{\rho}_{\mathrm{C}}(1)\ldots\widehat{\rho}_{\mathrm{C}}(n) >_{\mathrm{GC}} \; , & \text{(2.15a)} \\ G_\varphi^{(n)}(1,\ldots,n) &= \; <\varphi(1)\ldots\varphi(n) >_{\mathcal{H}} \; , & \text{(2.15b)}\end{aligned}$$

where, in equation (2.15a), the microscopic charge density $\widehat{\rho}_{\mathrm{C}}$ is given by

$$\begin{aligned}\widehat{\rho}_{\mathrm{C}}(1) &= \; \tau(1,2) \, q_\alpha\widehat{\rho}_\alpha(2) \; , \\ \widehat{\rho}_\alpha(\boldsymbol{r}) &= \; \sum_{i=1}^{N_\alpha}\delta^{(3)}(\boldsymbol{r} - \boldsymbol{r}_i^\alpha) \; ,\end{aligned} \tag{2.16}$$

the summation over the dummy indices α being understood in the first line of equation (2.16). It proves convenient to define also the truncated (or connected) n-body correlation functions by the relations

$$\begin{aligned}G_{\mathrm{C}\,(\varphi)}^{(1)\,\mathrm{T}}(1) &= \; G_{\mathrm{C}\,(\varphi)}^{(1)}(1) \; , \\ G_{\mathrm{C}\,(\varphi)}^{(n)\,\mathrm{T}}(1,\ldots,n) &= \; G_{\mathrm{C}\,(\varphi)}^{(n)}(1,\ldots,n) - \sum\prod_{m<n} G_{\mathrm{C}\,(\varphi)}^{(m)\,\mathrm{T}}(i_1,\ldots,i_m) \text{ for } n \geq 2 \; ,\end{aligned} \tag{2.17}$$

where the sum of products is carried out over all possible partitions of the set $(1,\ldots,n)$ into subsets of cardinality $m < n$[27]. The relations between the truncated $G_{\mathrm{C}}^{(n)\,\mathrm{T}}$ and $G_\varphi^{(n)\,\mathrm{T}}$ were obtained in ref. (11) by a lengthy and cryptic method, a new simple derivation is given in appendix A. For a homogeneous system one finds at order $n = 0$ the charge neutrality condition, i.e.

$$\rho_{\mathrm{C}} = \rho_\alpha q_\alpha = 0 \; , \tag{2.18}$$

and, at higher orders, the following relations

$$\beta G_{\text{C}}^{(2)\,\text{T}}(1,2) \;=\; \frac{-1}{4\pi}\Delta_1\delta(1,2) - \frac{1}{(4\pi)^2}\Delta_1\Delta_2 G_\varphi^{(2)\,\text{T}}(1,2)\,, \tag{2.19a}$$

$$\beta^{n/2} i^n G_{\text{C}}^{(n)\,\text{T}}(1,\ldots,n) \;=\; \frac{(-1)^n}{(4\pi)^n}\Delta_1\ldots\Delta_n G_\varphi^{(n)\,\text{T}}(1,\ldots,n) \quad \text{for } n\geq 3\,. \tag{2.19b}$$

In ref. (11) we have computed the free energy $f(\{\rho_\alpha\})$ of the homogeneous SPM at the second loop order in the framework of the KSSHE field theory. Before giving and discussing this expression we want to stress that the exact $f(\{\rho_\alpha\})$ should be independent of the form of the pair potential $w(r)$ inside the core, i.e. of the type of regularization adopted for the KSSHE transform. More generally, each term of say a systematic low fugacity or high temperature expansion of $f(\{\rho_\alpha\})$ should also be independent of this regularization; this point was carefully checked in refs. (9,10) in the case of the RPM. However here, as in ref. (11), we consider a loop-wise expansion of $f(\{\rho_\alpha\})$. The small parameter involved in this expansion cannot be given a clear physical interpretation and serves only to keep track of certain classes of Feynman diagrams[13]. Consequently each term of the loop expansion depends upon $w(r)$ inside the core. Deciding which type of regularization to adopt is a matter of arbitrariness or mathematical skill. However it seems reasonable to impose that, at each order of the loop expansion, $f(\{\rho_\alpha\})$ should be stationary with respect to the variations of $w(r)$ inside the core.

The zero-loop (mean-field (MF) or tree level), one-loop and two-loops expressions of $f(\{\rho_\alpha\})$ will be denoted by $f^{(0)}$, $f^{(1)}$, and $f^{(2)}$ respectively. Although the expressions obtained for $f^{(0)}$, $f^{(1)}$, and $f^{(2)}$ in ref. (11) were derived with the assumption of a charge smearing regularization for $w(r)$ one can safely assume that they remain valid for any reasonable regularization of $w(r)$ inside the HS core (i.e. such that $\widetilde{w}(k) > 0$ and $w(r) = 1/r$ for $r > \sigma$).

B. Zero-loop order

For a homogeneous system one finds for the zero-loop free energy per unit volume the sloppy result[11]

$$\beta f^{(0)}(\{\rho_\alpha\}) = \beta f_{\text{HS}}(\{\rho_\alpha\}) - \frac{\beta}{2}\,\rho_\alpha q_\alpha^2\,w(0)\,, \tag{2.20}$$

where $f_{\text{HS}}(\{\rho_\alpha\})$ denotes the excess free energy per unit volume of the reference HS fluid. Moreover the charge neutrality condition $\rho_\alpha q_\alpha = 0$ has to be be satisfied[11]. Note that $\beta f^{(0)}$ diverges to $-\infty$ for a point like distribution $\tau(r) = \delta^{(3)}(\boldsymbol{r})$ but remains finite after regularization if $w(r)$ is well behaved a $r = 0$. Although disappointingly simple, equation (2.20) can be however exploited for it can be shown that the MF free energy $\beta f^{(0)}(\{\rho_\alpha\})$ constitutes an exact lower bound for the exact free energy $f(\{\rho_\alpha\})$[11]. Maximizing the expression (2.20) of $\beta f^{(0)}(\{\rho_\alpha\})$ with respect to he variations of $w(r)$ inside the core should yield an optimized lower bound for $f(\{\rho_\alpha\})$; unfortunately this mathematical problem has no solution since, as apparent from equation (2.20), $\beta f^{(0)}(\{\rho_\alpha\})$ is a linear functional of $w(r)$. However, if one restricts oneself to potentials of the form (2.2) the problem can be solved[11] and one finds that the distribution $\tau(r)$ which maximizes $\beta f^{(0)}(\{\rho_\alpha\})$ is a uniform surface distribution of charges of radius equal to that of the ions, i.e. the distribution $\tau_\sigma(r)$ given by equation (2.3) with $a \equiv \sigma$, whence the optimized lower bound $\beta f_{\text{HS}}(\{\rho_\alpha\}) - \beta\rho_\alpha q_\alpha^2/\sigma$ for the free energy, i.e. nothing but the well known Onsager bound[1,28]. We christen this regularization scheme of $w(r)$ as the optimized mean field (OMF) scheme.

The pair correlation functions $h_{\alpha,\beta}^{(0)}(r) \equiv g_{\alpha,\beta}^{(0)}(r) - 1$ and the direct correlation functions $c_{\alpha,\beta}^{(0)}(r)$[1] at the zero-loop order are related to the free propagator $\Delta(r)$ of KSSHE field theory. In Fourier space one has[11]

$$\widetilde{h}_{\alpha,\beta}^{(0)}(k) \;=\; \widetilde{h}_{\text{HS},\,\rho}(k) - \beta q_\alpha q_\beta \widetilde{\Delta}(k)\,, \tag{2.21a}$$

$$\widetilde{c}_{\alpha,\beta}^{(0)}(k) \;=\; \widetilde{c}_{\text{HS},\,\rho}(k) - \beta q_\alpha q_\beta \widetilde{w}(k)\,, \tag{2.21b}$$

where $\widetilde{h}_{\text{HS},\,\rho}(k)$ and $\widetilde{c}_{\text{HS},\,\rho}(k)$ denote the Fourier transforms of the ordinary and direct correlation functions of a HS fluid at the density $\rho = \sum_\alpha \rho_\alpha$ respectively. We emphasize that $h_{\alpha,\beta}^{(0)}(r)$ and $c_{\alpha,\beta}^{(0)}(r)$, as given by equations (2.21), do satisfy to the Ornstein-Zernicke (OZ) relations[1]

$$h_{\alpha,\beta}^{(0)}(r) = c_{\alpha,\beta}^{(0)}(r) + \rho_\gamma c_{\alpha,\gamma}^{(0)} \star h_{\gamma,\beta}^{(0)}(r) \tag{2.22}$$

where the symbol "$\star$" denotes a convolution in space. The Fourier transform of the propagator has the following expression[11]

$$\widetilde{\Delta}(k) = \frac{\widetilde{w}(k)}{1 + \beta \, \rho_\alpha q_\alpha^2 \, \widetilde{w}(k)}. \tag{2.23}$$

Therefore $w(r)$ and $\Delta(r)$ also satisfy to an OZ-like equation in direct space, that is

$$\Delta(r) = w(r) - \beta \, [\rho_\alpha q_\alpha^2] \, \Delta \star w(r) \ . \tag{2.24}$$

We stress that the propagator $\Delta(r)$ as well as the correlation functions $h_{\alpha,\beta}^{(0)}(r)$ and $c_{\alpha,\beta}^{(0)}(r)$ do depend on the form of $w(r)$ inside the core.

C.   One-loop order

The one-loop free energy per unit volume is given by[11]

$$
\begin{aligned}
\beta f^{(1)}(\{\rho_\alpha\}) &= \beta f^{(0)}(\{\rho_\alpha\}) + \frac{1}{2} \int \frac{d^3\boldsymbol{k}}{(2\pi)^3} \, \ln(1 + \beta[\rho_\alpha q_\alpha^2]\widetilde{w}(k)) \\
&= \beta f_{\mathrm{HS}}(\{\rho_\alpha\}) + \frac{1}{2} \int \frac{d^3\boldsymbol{k}}{(2\pi)^3} \, \left[\ln\left(1 + \beta[\rho_\alpha q_\alpha^2]\widetilde{w}\,(k)\right) - \beta[\rho_\alpha q_\alpha^2]\widetilde{w}\,(k)\right] \ .
\end{aligned} \tag{2.25}
$$

$\beta f^{(1)}$ obviously still depends on the pair potential $w(r)$ inside the core but we note by passing that the expression (2.25) of $\beta f^{(1)}(\{\rho_\alpha\})$ remains finite (contrary to that of $\beta f^{(0)}$) for point-like distributions of charges, i.e. for $\tau_{\mathrm{DH}}(r) = \delta^{(3)}(\boldsymbol{r})$. One indeed obtains in this case the well-known Debye-Hückel (DH) result

$$\beta f_{\mathrm{DH}}(\{\rho_\alpha\}) = \beta f_{\mathrm{DH}}(\{\rho_\alpha\}) - \frac{\kappa^3}{12\pi} \ , \tag{2.26}$$

where $\kappa^2 = 4\pi\beta \, \rho_\alpha q_\alpha^2$ is the squared Debye number. Incidently the DH propagator can also be computed with the result

$$\Delta_{\mathrm{DH}}(r) = \exp(-\kappa r)/r \ . \tag{2.27}$$

In the Gaussian approximation the free energy is given by its one-loop expression (2.25) and the correlation functions by their zero-loop expressions (2.21)[11,12]. The Gaussian approximation of the KSSHE field theory therefore coincides exactly with the usual random phase approximation (RPA) of the theory of liquids[1,29]. One can further demand the one-loop free energy $\beta f^{(1)}(\{\rho_\alpha\})$ to be independent of the expression of $w(r)$ inside the core. As well known the stationary condition

$$\frac{\delta \beta f^{(1)}(\{\rho_\alpha\})}{\delta w(\boldsymbol{r})} = 0 \text{ for } r \leq \sigma \ , \tag{2.28}$$

yields the conditions $g_{\alpha,\beta}^{(0)}(r)$ for $0 \leq r \leq \sigma$ and for all pairs (α, β). We recover in that way the optimized random phase approximation (ORPA) of the theory of liquids[1,29]. It follows from eqs. (2.21) that the condition of nullity of $g_{\alpha,\beta}^{(0)}(r)$ inside the core can be rewritten as

$$
\begin{aligned}
w(r) &= 1/r \text{ for } r \geq \sigma \\
\Delta(r) &= 0 \text{ for } r \leq \sigma \ ,
\end{aligned} \tag{2.29}
$$

where $w(r)$ and $\Delta(r)$ are linked by the integral equation (2.24). Note that this equation does not involve the correlation functions of the reference HS system and that it also appears in the mean spherical approximation (MSA) of the SPM (in this case the exact correlation functions h_{HS} and c_{HS} in the right hand side of eqs. (2.21) have to be replaced by their Percus-Yevick (PY) expressions , i.e. h_{PY} and c_{PY} respectively[1]). It turns out that equations (2.24) and (2.29) can be solved analytically with the result[1,30]

$$w_{\mathrm{MSA}}(r) = 1/r \text{ for } r \geq \sigma \ , \tag{2.30a}$$

$$w_{\mathrm{MSA}}(r) = \frac{B}{\sigma} \, (2 - \frac{Br}{\sigma}) \text{ for } 0 \leq r \leq \sigma \ , \tag{2.30b}$$

$$B = \frac{x^2 + x - x(1 + 2x)^{1/2}}{x^2} \ , \tag{2.30c}$$

where $x = \kappa\sigma$. We remark that the function $w_{\text{MSA}}(r)$ meets all the requirements of a regularized potential, i.e. $w_{\text{MSA}}(r) = 1/r$ for $r \geq \sigma$ and $\widetilde{w}(k) \geq 0$ as can be shown easily, and therefore can be used as a regularizator of the KSSHE transform. It must be stressed that, despite of the formal analogies between equations (2.30b) and (2.4) -the latter being deduced from the former by setting $B = 1$-, $w_{\text{MSA}}(r)$ cannot be interpreted as the interaction energy between two smeared distributions of charge since $0 < B < 1$ as discussed in ref.(11). The same function $w_{\text{MSA}}(r)$ appears in the MSA and ORPA approximations for the SPM and yields in both cases ion-ion pair correlation functions which vanish inside the HS core. By contrast, the regularized potential $w_\sigma(r)$ which enters the OMF free energy does not insure the nullity of $g_{\alpha,\beta}^{(0)}(r)$ for $r \leq \sigma$.

With the choice $w(r) \equiv w_{\text{MSA}}(r)$ the one-loop free energy (2.25) can be computed exactly. The result is well-known[30] but we cannot refrain from giving the following derivation which seems to be original. Let us first compute the internal energy per unit volume $u_{\text{ORPA}} = \partial\beta f_{\text{ORPA}}(\{\rho_\alpha\})/\partial\beta$. It follows from equation (2.25) that

$$
\begin{aligned}
u_{\text{ORPA}} &= -\frac{1}{2}\int \frac{d^3\boldsymbol{k}}{(2\pi)^3}\,\beta\,[\rho_\alpha q_\alpha^2]\,\widetilde{\Delta}_{\text{MSA}}(k)\,\frac{\partial}{\partial\beta}\left[\beta\,[\rho_\alpha q_\alpha^2]\,\widetilde{w}_{\text{MSA}}(k)\right]\\
&= -\frac{1}{2}\int d^3\boldsymbol{r}\,\beta\,[\rho_\alpha q_\alpha^2]\,\Delta_{\text{MSA}}(r)\frac{\partial}{\partial\beta}\left[\beta\,[\rho_\alpha q_\alpha^2]\,w_{\text{MSA}}(r)\right]\;,
\end{aligned}
\tag{2.31}
$$

where we made use of the expression (2.23) of $\widetilde{\Delta}(k)$. Since the propagator $\Delta_{\text{MSA}}(r)$ vanishes inside the core in the ORPA (and MSA) approximations we have merely to compute the derivative of $\beta\,[\rho_\alpha q_\alpha^2]\,w_{\text{MSA}}(r)$ with respect to β for $r > \sigma$ which is trivial since $w_{\text{MSA}}(r) = 1/r$ in this case. Therefore

$$
\begin{aligned}
u_{\text{ORPA}} &= -\frac{\beta}{2}\,[\rho_\alpha q_\alpha^2]\int d^3\boldsymbol{r}\,\Delta_{\text{MSA}}(r)\,[\rho_\alpha q_\alpha^2]\,w_{\text{MSA}}(r)\\
&= \frac{\beta}{2}\,[\rho_\alpha q_\alpha^2]\left(\Delta_{\text{MSA}}(r=0) - w_{\text{MSA}}(r=0)\right)\;,
\end{aligned}
\tag{2.32}
$$

where we made use of equation (2.24) to obtain the last line. Since $\Delta_{\text{MSA}}(0) = 0$, we have finally

$$
\begin{aligned}
u_{\text{ORPA}} &= \frac{-\beta}{2}\,[\rho_\alpha q_\alpha^2]\,w_{\text{MSA}}(0)\;,\\
&= -\beta\,[\rho_\alpha q_\alpha^2]\,B/\sigma\;,\\
&= -\frac{x^2 + x - x(1+2x)^{1/2}}{4\pi\beta\sigma^3}\;,
\end{aligned}
\tag{2.33}
$$

which leads, after integration, to the ORPA free energy[1,29,30]

$$
\begin{aligned}
\beta f_{\text{ORPA}}(\{\rho_\alpha\}) &= \beta f_{\text{HS}}(\{\rho_\alpha\}) + \int_0^\beta d\beta'\,u_{\text{ORPA}}(\beta')\\
&= \beta f_{\text{HS}}(\{\rho_\alpha\}) - \frac{3x^2 + 6x + 2 - 2(1+2x)^{1/2}}{12\pi\sigma^3}\;.
\end{aligned}
\tag{2.34}
$$

D. Two-loop order

The free energy of the SPM at the second-loop order has the following expression[11]

$$
\begin{aligned}
\beta f^{(2)}(\{\rho_\alpha\}) &= \beta f^{(1)}(\{\rho_\alpha\}) - \frac{\beta^2}{4}[\rho_\alpha q_\alpha^2]^2\int d^3\boldsymbol{r}\,h_{\text{HS},\,\rho}(r)\Delta^2(r)\\
&\quad + \frac{\beta^3}{12}[\rho_\alpha q_\alpha^3]^2\int d^3\boldsymbol{r}\,\Delta^3(r)\;,
\end{aligned}
\tag{2.35}
$$

where $h_{\text{HS},\,\rho}(r)$ denotes the usual pair correlation function of a fluid of a single species of hard spheres at the total number density $\rho = \sum_\alpha \rho_\alpha$. Demanding the independence of $\beta f^{(2)}(\{\rho_\alpha\})$ with respect to the variations of $w(r)$ inside the core is a formidable mathematical task that cannot be achieved analytically. Each of the regularization schemes that we have discussed previously can be considered however, yielding different expressions for the propagator $\Delta(r)$ and thus for $\beta f^{(2)}$. Expression (2.35) remains however tractable, at least numerically, since it involves integrals of the functions $\Delta(r)$ and $h_{\text{HS},\,\rho}(r)$ which can be both evaluated numerically (for instance, the approximation $h_{\text{HS},\,\rho}(r) \sim h_{\text{PY},\,\rho}(r)$ can be used safely at low and moderate densities).

E.   The WCA regularization scheme

We end this section by discussing briefly the popular Weeks-Chandler-Andersen (WCA) regularization scheme. In the WCA scheme the potential $w(r)$ inside the core is assumed to be a constant equal to $1/\sigma$[31]. Clearly it amounts to define $w(r)$ as the electric potential created by a uniform surface distribution of charge $\tau_\sigma(r)$ where $\tau_\sigma(r)$ is the distribution defined at equation (2.3) with $a = \sigma$. It follows from this remark that the Fourier transform of the regularized pair potential reads as

$$\widetilde{w}_{\text{WCA}}(k) = \frac{4\pi\widetilde{\tau}_\sigma(k)}{k^2}$$

with $\widetilde{\tau}_\sigma = \sin(k\overline{\sigma})/(k\overline{\sigma})$. Therefore $\widetilde{w}_{\text{WCA}}(k)$ is not positive for all k and the KSSHE transformation is ill-defined. As a consequence the propagator $\Delta_{\text{WCA}}(r)$ can be singular (cf equation (2.23)). This singularity yields the so-called RPA catastrophe[1] for the one-loop (RPA) free energy since the argument of the ln in the RHS of equation (2.25) can become negative. This finite wave-number k instability, which however is absent in the OMF and MSA regularization schemes, has been made responsible of the possible existence of charge-ordered phase[19,20,21,24]. Although an order-disorder transition of the lattice-version of the RPM was indeed observed in Monte Carlo simulations[32,33], the evidences of a similar transition for the off-lattice version of the model are lacking at the time of writing as far as the author is well informed.

III.   THE BINARY MIXTURE

In this section we specialize the results of section II to the case of a binary mixture ($M = 2$). The cations and the anions have all the same diameter σ and bear charges $q_1 = q$ and $q_2 = -\xi q$ respectively where ξ is the charge assymetry parameter. It follows from the neutrality condition (2.18) that the ion densities are $\rho_1 = \xi\rho/(1 + \xi)$ and $\rho_2 = \rho/(1 + \xi)$ where $\rho = \rho_1 + \rho_2$ is the total number density. For convenience we introduce the reduced densities $\rho_\alpha^\star = \rho_\alpha\sigma^3$ and free energies per unit volume $\overline{\beta f} = \beta f\sigma^3$. The reduced free energy $\overline{\beta f}_{\text{HS}}$ of the reference HS system is thus given by

$$\overline{\beta f}_{\text{HS}}(\rho_1^\star, \rho_2^\star) = \overline{\beta f}_{\text{HS}}(\rho^\star) + \rho^\star \left(\frac{\xi}{1 + \xi} \ln \xi - \ln(1 + \xi) \right) , \qquad (3.1)$$

where $\overline{\beta f}^{\text{HS}}(\rho^\star)$ is the free energy of a pure HS liquid at the reduced density $\rho^\star$. The additional term in the RHS of equation (3.1) corresponds to the mixing entropy contribution. Following the authors of ref. (34) we define the reduced inverse temperature $\beta^\star \equiv \beta q^2 \xi/\sigma$ and the reduced temperature as $T^\star = 1/\beta^\star$. The reduced Debye number will of course be defined as $\kappa^\star = \kappa\sigma$ (note that $\kappa^{\star 2} = 4\pi\beta^\star\rho^\star$) and we will also frequently make use of the dimensionless squared Debye number $\lambda = \kappa^{\star 2}$.

Quite remarkably the electrostatic contribution to the one-loop free energy depends solely on parameter λ and *not* on the charge asymmetry factor ξ. Indeed one has

$$\overline{\beta f}^{(1)} = \overline{\beta f}_{\text{HS}}(\rho^\star) + \rho^\star \left(\frac{\xi}{1 + \xi} \ln \xi - \ln(1 + \xi) \right) + I[\lambda] , \qquad (3.2)$$

where the expression of the function $I[\lambda]$ depends on the choice of regularization made for $w(r)$. The expressions of $I[\lambda]$ in the DH and ORPA schemes have been given at eqs. (2.26) and (2.34) respectively. In the OMF and WCA schemes one has

$$I_{\text{OMF}}[\lambda] = \frac{2}{\pi^2} \int_0^\infty dx\, x^2 \left(\ln\left(1 + \frac{\lambda}{4} \frac{\sin x^4}{x^4} \right) - \frac{\lambda}{4} \frac{\sin x^4}{x^4} \right) , \qquad (3.3a)$$

$$I_{\text{WCA}}[\lambda] = \frac{1}{4\pi^2} \int_0^\infty dx\, x^2 \left(\ln\left(1 + \frac{\lambda}{x^3} \sin x \right) - \frac{\lambda}{x^3} \sin x \right) , \qquad (3.3b)$$

respectively. Both integrals occurring in eqs (3.3) are convergent at $x = 0$ and $x = \infty$ and can be handled numerically easily. However, the second integral (3.3b) is singular for large values of λ (the so-called RPA catastrophe) since the argument of the ln can become negative at finite x. The stability limit is found to be $\lambda \leq \lambda_{\text{max.}} \sim 84.2$.

In the case of a regularization by a surface distribution of charges of radius $\overline{a} \equiv a/2 \leq \overline{\sigma}$ one has simply $I_a[\lambda] = I_\sigma[\lambda\overline{a}^2]\overline{a}^{-3} \equiv I_{\text{OMF}}[\lambda\overline{a}^2]\overline{a}^{-3}$. It is easy to check that in the point-like limit $a \to 0$ one gets $I_a[\lambda] \to -\lambda^{3/2}/12$, which coincides with the DH result (2.26) as expected.

At the two-loop order the free energy depends now not only on λ but also on the density and the charge asymmetry parameter ξ. One deduces from equation (2.35) that

$$\overline{\beta f}^{(2)} = \overline{\beta f}^{(1)} - \frac{1}{4} K[\lambda, \rho^\star] + \frac{1}{12} \frac{(1-\xi)^2}{\xi} L[\lambda, \rho^\star] , \tag{3.4}$$

with

$$K[\lambda, \rho^\star] = \int_0^\infty dx \, 4\pi x^2 \, \overline{\Delta}_\lambda^2(x) \, h_{\mathrm{HS}, \, \rho}(x) , \tag{3.5a}$$

$$L[\lambda, \rho^\star] = \frac{1}{\rho^\star} \int_0^\infty dx \, 4\pi x^2 \overline{\Delta}_\lambda^3(x) , \tag{3.5b}$$

where $x = r/\sigma$ is the distance in reduced units and $\overline{\Delta}_\lambda(x) \equiv \beta^\star \rho^\star \sigma^{-2} \Delta_\lambda(r = \sigma x)$ is the reduced propagator. We stress once again that, since Δ_λ is simply related to the pair potential w (cf equations (2.23), and (2.24)) it depends therefore on the regularization scheme. For a given regularization scheme it depends only upon the parameter λ. Moreover, we note that $\overline{\beta f}^{(2)}$ is invariant under the transform $\xi \to 1/\xi$ as expected and that the second term in the RHS of equation (3.4) vanishes in the case of the RPM ($\xi = 1$). Expressions (3.5a) and (3.5b) can easily be computed numerically for each regularization scheme (for numerical details see Appendix B).

IV. THE LIQUID-VAPOR TRANSITION OF THE BINARY SPM

A. Theoretical background

In past recent years extensive Monte Carlo simulations have been performed to study the liquid-vapor transition of the RPM and to elucidate the nature of ionic criticality. It seems now well established that the critical exponents of the RPM are those of the $3D$ Ising model[35,36,37,38]. The more recent estimates of the Orsay group for the critical temperature, density, and chemical potentials are[38] $T_c^\star = 0.04917 \pm 0.00002$, $\rho_c^\star = 0.080 \pm 0.005$, and $\nu_c^\star = -13.600 \pm 0.005$ respectively (the critical pressure is not known with accurate precision). Recent numerical studies are also available for binary mixtures with an asymmetry in charge or/and in size[34,39].

Here we consider only the binary SPM and study various MF theories built with the approximate free energies discussed in section III. We work in the framework of the Landau theory with a Landau function given by the expression[25]

$$w(\nu, \beta, \varphi) = \beta f(\beta, \varphi) - \nu \varphi , \tag{4.1}$$

the minimum of which gives minus the MF pressure, i.e.[25]

$$-\beta P_{\mathrm{MF}}(\nu, \beta) = \min_\varphi w(\nu, \beta, \varphi) . \tag{4.2}$$

Note that φ plays the role of the order parameter of the Landau theory. The free energy function $\beta f(\beta, \varphi)$ which enters equation (4.1) can be rewritten as

$$\beta f(\beta, \varphi) = \beta f_{\mathrm{HS}}(\varphi) - \varphi \left(\frac{\xi}{1+\xi} \ln \xi - \ln(1+\xi) \right) + J(\lambda, \varphi) , \tag{4.3}$$

where

$$J(\lambda, \varphi) = I(\lambda) - \frac{1}{4} K(\lambda, \varphi) + \frac{1}{12} \frac{(1-\xi)^2}{\xi} L[\lambda, \varphi] . \tag{4.4}$$

$\beta f_{\mathrm{HS}}(\varphi)$ is the free energy of the HS reference system as given by equation (3.1) and the functions I, K, and L in the RHS of equation (4.4) are those defined in section III. Note that we have dropped all the "$\star$" to simplify the notations, reduced quantities are implicitly meant.

Above T_c and for any chemical potential ν, $w(\nu, \beta, \varphi)$ is a convex function of the order parameter φ and equation (4.2) admits a unique solution $\overline{\varphi}(\nu, \beta)$ which is the (unique) solution of the stationary condition

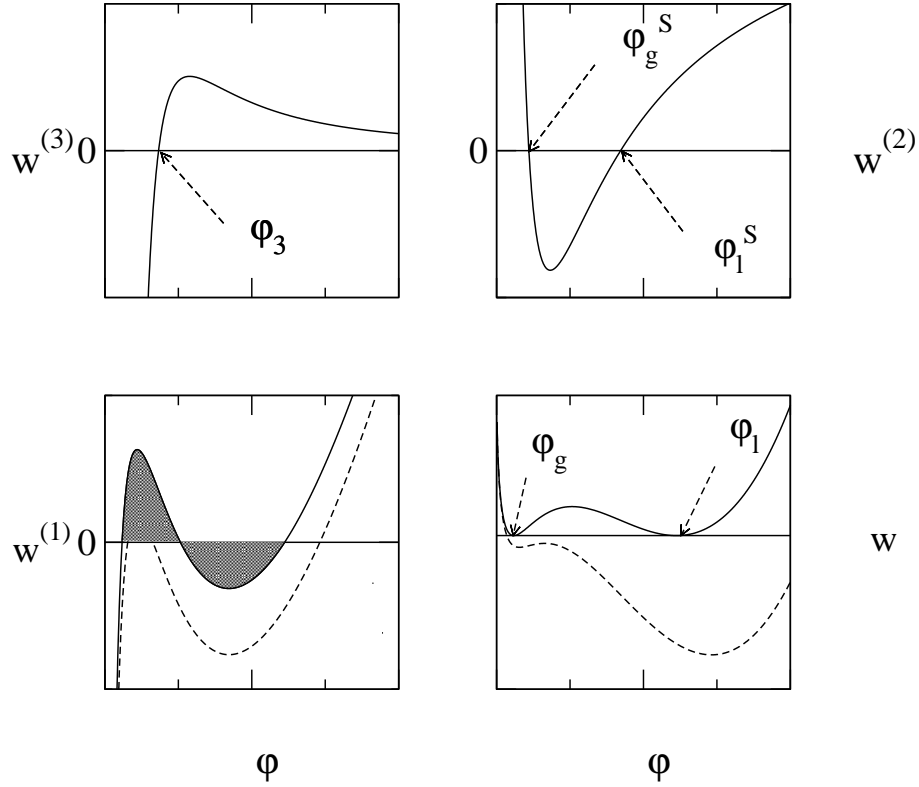$$\left. \frac{\partial w}{\partial \varphi} \right|_{\overline{\varphi}} = 0 . \tag{4.5}$$

FIG. 1: The Landau function $w(\varphi)$ and its first three derivatives $w^{(n)}(\varphi)$ at $T < T_c$. The functions $w^{(2)}$ and $w^{(3)}$ are independent of the chemical potential. The zeros of $w^{(2)}$ give the spinodal densities. $w^{(1)}$ and w are diplayed for arbitrary ν (dashed curves) and for $\nu = \nu_{\mathrm{coex}}$ (solid curves). At the coexistence the grayish areas are equal.

Therefore the MF pressure is given by $\beta P_{\mathrm{MF}}(\nu, \beta) = -w(\nu, \beta, \overline{\varphi})$ which yields the expressions of the MF densities and energies per unit volume

$$\rho_{\mathrm{MF}}(\nu, \beta) \;=\; \frac{\partial \beta P_{\mathrm{MF}}}{\partial \nu} = \overline{\varphi} \;, \tag{4.6a}$$

$$u_{\mathrm{MF}}(\nu, \beta) \;=\; -\frac{\partial \beta P_{MF}}{\partial \beta} = 4\pi \overline{\varphi} \, \frac{\partial J}{\partial \lambda}(\lambda, \overline{\varphi}) \;, \tag{4.6b}$$

where we made use of the stationary condition (4.5).

Below T_c, $w(\nu, \beta, \varphi)$ is no longer a convex function of φ and a second minimum of $w(\nu, \beta, \varphi)$ arises for some range of chemical potentials. For $T < T_c$ ($\beta > \beta_c$) there is a unique chemical potential $\nu_{\mathrm{coex}}(\beta)$ corresponding to two values $\overline{\varphi}_g$ and $\overline{\varphi}_l > \overline{\varphi}_g$ such that $-\beta P_{\mathrm{MF, \, coex}}(\beta) = w(\nu_{\mathrm{coex}}, \beta, \overline{\varphi}_g) = w(\nu_{\mathrm{coex}}, \beta, \overline{\varphi}_l)$ (see figure (1)). These two minima corresponds to the coexistence of a gas phase at the density $\rho_{\mathrm{MF, \, g}}(\beta) = \overline{\varphi}_g$ and a liquid at the density $\rho_{\mathrm{MF, \, l}}(\beta) = \overline{\varphi}_l$. At the critical temperature the two solutions $\overline{\varphi}_g$ and $\overline{\varphi}_l$ merge into a unique solution $\overline{\varphi}_c = \rho_{\mathrm{MF, \, c}}$ corresponding to the critical density.

We have determined numerically the coexistence curve of the SPM for the one-loop and two-loop expressions of the free energy for various regularizations schemes discussed in section II, i.e.

- charge smearing regularization scheme (i.e. $w(r) = w_a(r)$). We limited ourselves to the case of the surface distribution (2.3) with $a^* = a/\sigma$ ranging from 0 (DH case) to 1 (OMF case).

- MSA regularization scheme (i.e. $w(r) = w_{\mathrm{MSA}}(r)$).

- WCA regularization scheme (i.e. $w(r) = w_{\mathrm{WCA}}(r)$, cf sec. (II E)). In this case a numerical solution was obtained only for temperatures not to far below T_c in order to avoid the RPA catastrophe.
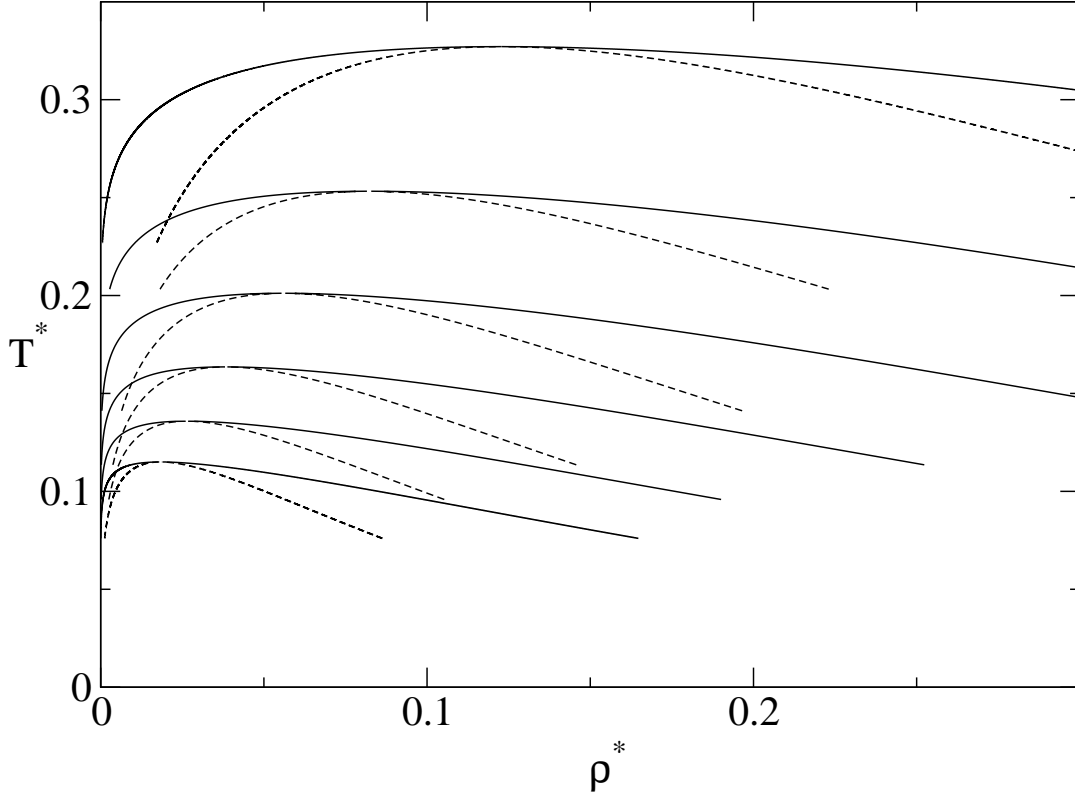
FIG. 2: Coexistence curves of the RPM in the one-loop approximation with $w(r) = w_a(r)$. From top to bottom $a^* = 0$ (DH), $a^* = 0.2$, $a^* = 0.4$, $a^* = 0.6$, $a^* = 0.8$, $a^* = 1$ (OMF). Solid lines : coexistence curves, dashed line: spinodal curves.

B. Numerical results

We have found worthwhile to discuss shortly the algorithm devised to obtain the coexistence curve in appendix B. The results for the critical temperatures, chemical potentials, pressures, densities and energies are summarized in tables (I, II, III) and are discussed below.

1. One-loop results

We have already noticed that the free energy of the binary SPM is independent of the charge assymetry factor ξ at the one-loop order. The coexistence curves and notably the critical parameters (T_c^*, ρ_c^*, ...etc) are therefore independent of ξ which is a serious drawback clearly in contradiction with numerical simulation results[34,39].

Our data for the one-loop approximation are reported in table (I). In the case of the MSA regularization scheme one recovers the MSA theory provided that the HS free energy is chosen to be that of the PY approximation. In this case we observed a perfect agreement of our data those obtained by Gonzales-Tovar[41]. We stress that the results reported in table (I) for the MSA regularization scheme were obtained, as all other results reported in all the tables of this paper, by making use of the Carnahan-Starling approximation for the HS free energy and of the PY solution $h_{\mathrm{PY}}(r)$ of the HS corelation function.

As apparent in table (I) and figures (2) and (3) the coexistence curves depend strongly upon the regularization scheme adopted for the Coulomb potential inside the HS core. This is particularly striking for the charge smearing regularization scheme where the critical temperature T_c^* decreases steadily from $T_c^* = 0.3271$ for $a^* = 0$ (DH case) to $T_c^* = 0.1150$ for $a^* \equiv a/\sigma = 1$ (OMF case). Similarly the critical density ρ_c^* decreases with the diameter a of the charge distribution from $\rho_c^* = 0.12267$ for $a^* = 0$ to $\rho_c^* = 0.02198$ for $a^* = 1$.

The coexistence curves at the one-loop order obtained with the OMF, WCA, and MSA (or ORPA) regularization schemes are displayed in figure (3). The MSA scheme gives the better critical temperature, i.e. $T_c^{* \, \mathrm{MSA}} = 0.07858$ to be compared with the exact $T_c^* = 0.04917(2)$[38], whereas the critical density is largely underestimated, i.e. $\rho_c^{* \, \mathrm{MSA}} = 0.01449$ to be compared with the exact $\rho_c^* = 0.080(5)$[38]. By contrast the OMF scheme gives a slightly better critical
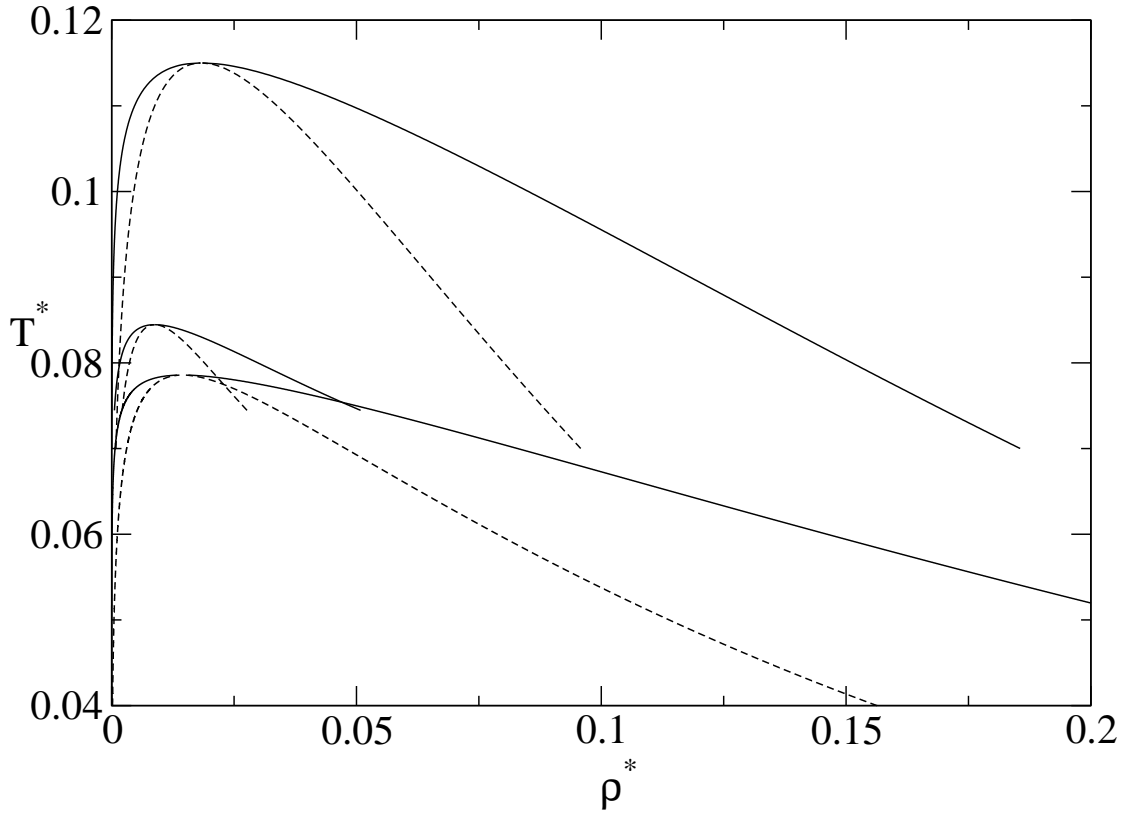
FIG. 3: Coexistence curves of the RPM in the one-loop approximation. From top to bottom: OMF scheme, WCA scheme, MSA scheme. Solid lines : coexistence curves, dashed line: spinodal curves.

density than the MSA scheme - however still largely underestimated-, i.e. $\rho_c^{*\,\mathrm{OMF}} = 0.01834$, but overestimates T_c^*, i.e $T_c^{*\,\mathrm{OMF}} = 0.1150$. The results obtained in the framework of the WCA scheme lie somewhere between those obtained via the OMF and MSA schemes.

2. Two-loop results

The critical parameters of the RPM at the two-loop order are given in table (II) and the coexistence curves are sketched in figure (4). Including the two-loop correction yields a slight decrease of the critical temperature in all cases (except for the MSA case) as well as an increase of the critical density. More precisely one finds, at the two-loop level, the following critical parameters : $(T_c^{*\,\mathrm{OMF}} = 0.1133, \ \rho_c^{*\,\mathrm{OMF}} = 0.0316)$, $(T_c^{*\,\mathrm{MSA}} = 0.07993, \ \rho_c^{*\,\mathrm{MSA}} = 0.01722)$, and $(T_c^{*\,\mathrm{WCA}} = 0.08428, \ \rho_c^{*\,\mathrm{WCA}} = 0.0137)$ in the OMF, MSA, and WCA schemes respectively. The improvement upon one-loop results is therefore significant but the theoretical predictions, notably those for the critical densities, are still far from the MC results. Our theoretical results can be (unfavorably) compared with those obtained recently in the framework of the the so-called collective variable (CV) method developed by the Ukrainian school which yield $(T_c^* = 0.0502, \ \rho_c^* = 0.042)$[22,24]. At the moment the relation between the CV method and the KSSHE formalism is not established, work in this direction in under way.

At the two-loop order the free energy of the binary SPM depends explicitly on the charge assymetry factor ξ. The effects of ξ on the coexistence curve parameters in the OMF, WCA, and MSA schemes are resumed in table (III) for $\xi = 1, 2, 3, 4, 5$. In all the considered regularization schemes the critical temperature T_c^* is found to increase slightly with ξ in clear contradiction with MC simulation data where a rapid decrease of T_c^* with ξ has been observed[34]. However, as apparent in table (II), the critical densities -despite much too low values- are found to increase slightly with ξ in the OMF and MSA schemes, which is in qualitative agreement with the MC data of ref. (34).
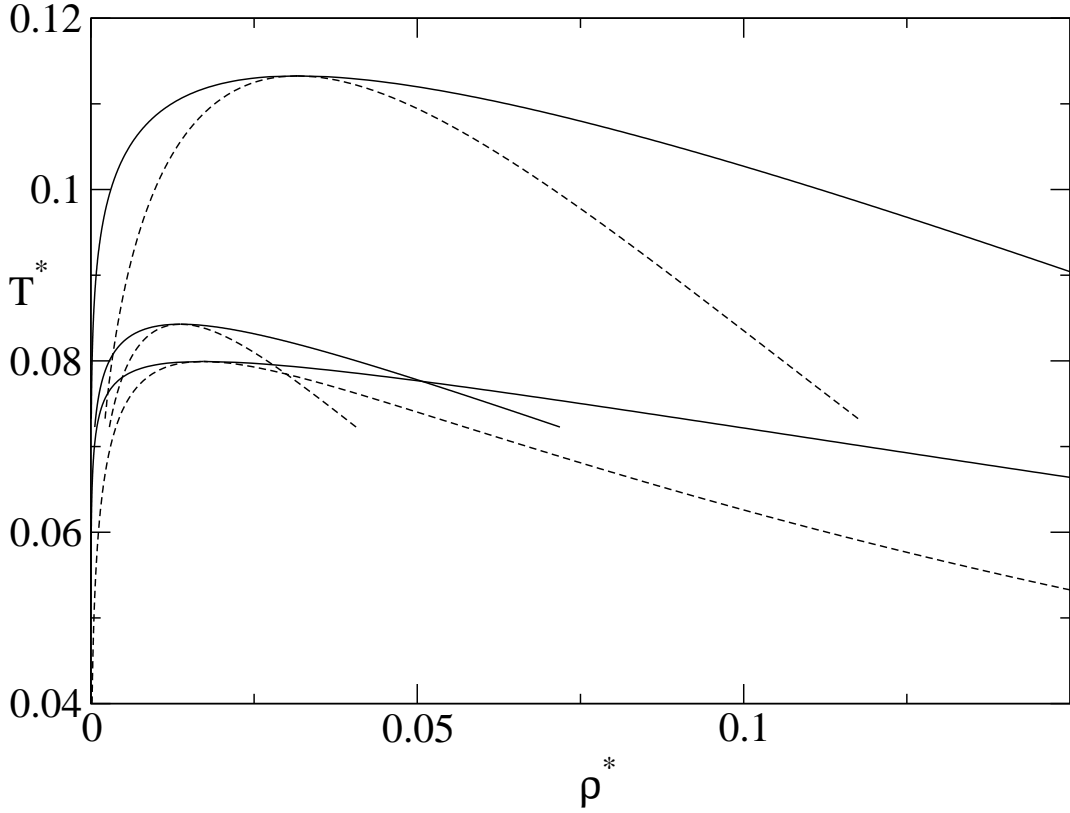
FIG. 4: Coexistence curves of the RPM in the two-loop approximation. From top to bottom: OMF scheme, WCA scheme, MSA scheme. Solid lines : coexistence curves, dashed line: spinodal curves.

V. SUMMARY

In this paper we have studied the liquid-vapor coexistence curve of the SPM -i.e. a simple version of the primitive model, the prototype of a system governed by long range Coulomb interactions-, by means of various mean-field theories. These theories were obtained in the framework of the KSSHE field-theoretical representation of charged HS systems by means of a loop expansion of the free energy of the homogeneous system[11]. Some of these MF theories are equivalent to well known approximations of the theory of liquids such that the Debye-Hückel, or MSA (ORPA) theory, other were considered here for the first time. The results obtained for the critical point are in all cases in poor agreement with the MC simulations.

The peculiarity of ionic criticality is clearly seen in the KSSHE formalism. The zero-loop order of the KSSHE theory is unable to reproduce a liquid-vapor transition and provides merely the local charge neutrality condition[11]; the transition appears only at the one-loop order which is an unusual feature and suggests some kind of inconsistence of the KSSHE theory for ionic systems. The same remark holds for the other field-theoretical treatments of the SPM[19,20,21,22,24]. From the KSSHE side, further challenges are the derivation of the one-loop corrections to the density correlation functions and generalization of the two-loop expansions of the homogeneous free energy to the case of a PM with size assymetry.

Acknowledgments

APPENDIX A: THE RELATIONS BETWEEN $G_{\mathbf{C}}^{(n)\,\mathbf{T}}$ AND $G_{\varphi}^{(n)\,\mathbf{T}}$

We shall denote by $\Xi[\{\nu_\alpha\}, V_e]$ the GCPF of the SPM in the presence of an external electrostatic potential $V_e(1)$. The M dimensionless chemical potentials ν_α are assumed to be uniform. Let $\rho_e(1)$ be the external charge distribution

giving rise to $V_e(1)$. $V_e(1)$ and $\rho_e(1)$ are linked by the Poisson equation which can be written, with the help of the formal notations of sec. (II), as

$$v_c^{-1}(1,2)V_e(2) = \rho_e(1) . \tag{A1}$$

Obviously the charge correlation functions defined at equation (2.17) can be expressed as the functional derivatives

$$
\begin{aligned}
G_C^{(n)}(1,\ldots,n) &= \frac{(-1)^n}{\beta^n} \frac{1}{\Xi[\{\nu_\alpha\}]} \left. \frac{\delta^n \Xi[\{\nu_\alpha\}, V_e]}{\delta V_e(1)\ldots\delta V_e(n)} \right|_{V_e=0} , \\
G_C^{(n)\,T}(1,\ldots,n) &= \frac{(-1)^n}{\beta^n} \left. \frac{\delta^n \ln \Xi[\{\nu_\alpha\}, V_e]}{\delta V_e(1)\ldots\delta V_e(n)} \right|_{V_e=0} .
\end{aligned}
\tag{A2}
$$

Expressions similar to equations (A2) can be derived for the field correlation functions $G_\varphi^{(n)}$ and $G_\varphi^{(n)\,T}$ in the following way. Firstly, note that one has $\Xi[\{\nu_\alpha\}, V_e] \equiv \Xi[\{\nu_\alpha - q_\alpha \overline{V}_e\}]$ where the "smeared" field $\overline{V}_e$ is given by $\overline{V}_e(1) = \beta\tau(1,2)\,V_e(2)$. Therefore the expression (2.13) of Ξ can be written more explicitly as

$$\Xi[\{\nu_\alpha\}, V_e] = \mathcal{N}_{v_c}^{-1} \int \mathcal{D}\varphi \, \exp(-\frac{1}{2}\left\langle\varphi|v_c^{-1}|\varphi\right\rangle - \ln \Xi_{HS}\left[\{\overline{\nu}_\alpha + iq_\alpha(\phi - \overline{V}_e)\}\right]) . \tag{A3}$$

We now perform the change of variables

$$\varphi \to \varphi - i\beta^{1/2}V_e \tag{A4}$$

in equation (A3). The functional Jacobian is equal to one and this gives us, after taking the logarithm

$$\ln \Xi[\{\nu_\alpha\}, V_e] = \frac{\beta}{2}\left\langle V_e|v_c^{-1}|V_e\right\rangle + \ln \Xi^*[\{\nu_\alpha\}, B] , \tag{A5}$$

where $\ln \Xi^*[\{\nu_\alpha\}, B]$ is the KSSHE partition function (2.13) associated with the modified action

$$\mathcal{H}[\varphi] - B(1)\varphi(1) , \tag{A6}$$

where $B(1) \equiv i\beta^{1/2}v_c^{-1}(1,2)V_e(2)$ plays the role of an additional external magnetic field. As it is well known, the functionals $\Xi^*[\{\nu_\alpha\}, B]$ and $\ln \Xi^*[\{\nu_\alpha\}, B]$ are the generators of the ordinary and connected correlation functions of the KSSHE field φ respectively[13]. Therefore we have

$$
\begin{aligned}
G_\varphi^{(n)}(1,\ldots,n) &= \frac{1}{\Xi[\{\nu_\alpha\}]} \left. \frac{\delta^n \Xi^*[\{\nu_\alpha\}, B]}{\delta B(1)\ldots\delta B(n)} \right|_{B=0} \\
G_\varphi^{(n)\,T}(1,\ldots,n) &= \left. \frac{\delta^n \ln \Xi^*[\{\nu_\alpha\}, B]}{\delta B(1)\ldots\delta B(n)} \right|_{B=0} .
\end{aligned}
\tag{A7}
$$

Taking the functional derivative of both sides of equation (A5) with respect to V_e and noting that

$$\frac{\delta B(1)}{\delta V_e(2)} = i\beta^{1/2}v_c^{-1}(1,2) , \tag{A8}$$

one finds that

$$
\begin{aligned}
\rho_C(1) + \rho_e(1) &= -i\beta^{-1/2}v_c^{-1}(1,2) < \varphi(1) > \\
&\equiv \frac{i}{4\pi\beta^{1/2}}\Delta_1 < \varphi(1) > ,
\end{aligned}
\tag{A9}
$$

yielding the charge neutrality condition $\rho_C(1) = 0$ for a uniform system in the absence of external charge, since in that case $< \varphi(1) > =$ cte .

Taking twice the functional derivative of both sides of equation (A5) with respect to V_e in the limit $B \to 0$ yields readily

$$\beta G_C^{(2)\,T}(1,2) = \frac{-1}{4\pi}\Delta_1\delta(1,2) - \frac{1}{(4\pi)^2}\Delta_1\Delta_2 G_\varphi^{(2)\,T}(1,2) , \tag{A10}$$

where we made use of equations (A2), (A7), and (A8). Finally, continuing the process and differentiating equation (A5) n times ($n \geq 3$) one obtains

$$\beta^{n/2}i^n G_C^{(n)\,T}(1,\ldots,n) = \frac{(-1)^n}{(4\pi)^n}\Delta_1\ldots\Delta_n G_\varphi^{(n)\,T}(1,\ldots,n) . \tag{A11}$$

Equations (A9), (A10), and (A11) were obtained in a complicated way in ref. (11).

APPENDIX B: AN ALGORITHM TO DETERMINE THE COEXISTENCE CURVE

In this appendix we give some details on the algorithm used to obtain the coexistence curve of the SPM in the various approximation schemes considered in the paper. We denote by $w^{(n)}(\nu, \beta, \varphi)$ the n-th partial derivative of the Landau function with respect to the order parameter φ. For $n \geq 2$, $w^{(n)}(\nu, \beta, \varphi)$ is independent of the chemical potential ν as apparent from equation (4.1). At any temperature T the function $w^{(3)}(\beta, \varphi)$ versus φ has the shape depicted in figure (1), i.e. with a unique zero located at some φ_3. A precise numerical estimate of φ_3 can be obtained with the help of the bisection method. In that aim we used the routine RTBIS of Numerical Recipes[40]. More precisely

$$\varphi_3 = \text{RTBIS}(w^{(3)}, \varphi_{\min}, \varphi_{\max}, \epsilon) , \tag{B1}$$

where RTBIS seeks for the (unique) zero of $w^{(3)}(\varphi)$ in the prescribed interval $[\varphi_{\min}, \varphi_{\max}]$ with some arbitrary precision ϵ.

Therefore the function $w^{(2)}(\beta, \varphi)$ versus φ is convex for all β. For $T < T_c$ $w^{(2)}$ has the shape depicted in figure (1), i.e. with a unique negative minimum at $\varphi = \varphi_3$. For $T > T_c$ the minimum is positive and thus the critical temperature T_c is obtained by the condition $w^{(2)}(\beta_c, \varphi_3) = 0$. The zeros of $w^{(2)}(\varphi)$ for $T < T_c$ will be denoted φ_g^S and $\varphi_l^S > \varphi_g^S$. They are also easily obtained with the help of the bisection method, i.e.

$$\varphi_g^S = \text{RTBIS}(w^{(2)}, \varphi_{\min}, \varphi_3, \epsilon) ,$$
$$\varphi_l^S = \text{RTBIS}(w^{(2)}, \varphi_3, \varphi_{\max}, \epsilon) .$$

Since there the second derivative of the free energy with respect to φ (i.e. the density) vanishes, the locus of the points $(\varphi_g^S, \varphi_l^S)$ is the so-called spinodal curve[25].

The points $(\varphi_g^S, \varphi_l^S)$ correspond to the maximum and the minimum of the function $w^{(1)}(\varphi)$ respectively. For an arbitrary chemical potential $\nu \neq \nu_{\text{coex}}$ one is likely to find the dashed curves of $w^{(1)}(\varphi)$ and $w(\varphi)$ displayed in figure (1). One wants to find the coexistence chemical potential ν_{coex} such that the two minima of $w(\varphi)$ have the same value, i.e. to find for $w(\varphi)$ and $w^{(1)}(\varphi)$ the solid curves depicted in figure (1). This can be achieved conveniently and precisely by means of the following iterative process.

(i) First one needs an estimate of ν not too far from ν_{coex}. Denoting by $w_{\min}^{(1)}$ and $w_{\max}^{(1)}$ the values of the minimum and maximum of $w^{(1)}(\varphi)$ respectively one adopts for ν the new value $\nu \to \nu_0 = \nu + (w_{\min}^{(1)} + w_{\max}^{(1)})/2$ which ensures that now $w_{\min}^{(1)} = -w_{\max}^{(1)}$.

(ii) The zeros of $w^{(1)}(\varphi)$ in the intervals $[\varphi_{\min}, \varphi_g^S]$ and $[\varphi_l^S, \varphi_{\max}]$ are rough estimates of the coexistence densities. Denoting them by φ_g^0 and φ_l^0 respectively one has

$$\varphi_g^0 = \text{RTBIS}(w^{(1)}, \varphi_{\min}, \varphi_g^S, \epsilon) ,$$
$$\varphi_l^0 = \text{RTBIS}(w^{(1)}, \varphi_l^S, \varphi_{\max}, \epsilon) .$$

(iii) At this point we have found a ν_0 and two estimates φ_g^0 and φ_l^0 such that $w^{(1)}(\nu_0, \varphi_g^0) = w^{(1)}(\nu_0, \varphi_l^0) = 0$ but $w(\nu_0, \varphi_g^0) \neq w(\nu_0, \varphi_l^0)$ in general. It follows from equation (4.1) that if one defines

$$\nu_1 = \nu_0 + \frac{w(\nu_0, \varphi_l^0) - w(\nu_0, \varphi_g^0)}{\varphi_l^0 - \varphi_g^0} , \tag{B2}$$

then $w(\nu_1, \varphi_g^0) = w(\nu_1, \varphi_l^0)$ but $w^{(1)}(\nu_1, \varphi_{g,l}^0) \neq 0$. One then determines two new estimates of φ_l and φ_g as

$$\varphi_g^1 = \text{RTBIS}(w^{(1)}(\nu_1, \varphi), \varphi_{\min}, \varphi_g^S, \epsilon) ,$$
$$\varphi_l^1 = \text{RTBIS}(w^{(1)}(\nu_1, \varphi), \varphi_l^S, \varphi_{\max}, \epsilon) .$$

Now one has $w^{(1)}(\nu_1, \varphi_g^1) = w^{(1)}(\nu_1, \varphi_l^1) = 0$ and one computes again $w(\nu_1, \varphi_g^1)$ and $w(\nu_1, \varphi_l^1)$. If

$$|\frac{w(\nu_1, \varphi_g^1) - w(\nu_1, \varphi_l^1)}{w(\nu_1, \varphi_g^1) + w(\nu_1, \varphi_l^1)}| < \epsilon , \tag{B3}$$

where ϵ is the wanted precision, then the problem is numerically solved. If it is not the case then one sets $\nu_1 \to \nu_0$, $\varphi_{g,l}^1 \to \varphi_{g,l}^0$ and one goes back to point (iii). For any reasonable ϵ a few iterations are necessary to get the result with a precision ϵ.

We end this appendix by a few comments on the numerical calculation of w and its derivatives $w^{(n)}$. The HS free energy and its derivatives were computed in the Carnahan-Starling approximation[1]. We also tried the PY expressions (in the compressibility route) which makes little difference at the rather low densities considered here. Only the numerical estimate of the functions $K[\lambda, \varphi]$ (cf equation (3.5a)) which enter the free energy at the second-loop order needs additional comments. In order to compute $K[\lambda, \varphi]$ and its partial derivatives with respect to φ (note that $\lambda = 4\pi\beta\varphi$ does also depends on φ) we have used the PY solution for $h_{\mathrm{HS}, \varphi}$. For numerical purposes it is necessary to reexpress K in terms of the function $\gamma_{\mathrm{HS}, \varphi}(r) = h_{\mathrm{HS}, \varphi}(r) - c_{\mathrm{HS}, \varphi}(r)$ which is a continuous function of r. In the framework of PY theory analytical expressions can be obtained for the Fourier transform $\widetilde{\gamma}_{\mathrm{HS}, \varphi}$ and its derivatives with respect to φ with the help of a computer algebra package. $\gamma_{\mathrm{HS}, \varphi}(r)$ and its derivatives with respect to φ are then obtained as inverse numerical Fourier transforms.

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TABLE I: One-loop results for the critical temperature T_c, chemical potential ν_c, pressure P_c, density ρ_c, and energy u_c of the SPM. Various regularization schemes are considered, as explained in the text.

	T_c	ν_c	$10^2 \times \beta P_c$	ρ_c	$10 \times u_c$
DH	0.3271	-5.5274	2.4194	0.12267	-1.3316
τ_a : $a^* = 0.1$	0.2868	-5.8553	1.8336	0.10015	-0.9552
$a^* = 0.2$	0.2532	-6.1688	1.4052	0.08224	-0.6981
$a^* = 0.3$	0.2250	-6.4703	1.0860	0.06778	-0.5170
$a^* = 0.4$	0.2012	-6.7608	0.8453	0.05598	-0.3866
$a^* = 0.5$	0.1809	-7.0408	0.6622	0.04630	-0.2913
$a^* = 0.6$	0.1636	-7.3104	0.5220	0.03835	-0.2210
$a^* = 0.7$	0.1487	-7.5695	0.4141	0.03180	-0.1686
$a^* = 0.8$	0.1358	-7.8182	0.3307	0.02641	-0.1293
$a^* = 0.9$	0.1247	-8.0564	0.2659	0.02198	-0.09977
OMF	0.1150	-8.2843	0.2154	0.01834	-0.07745
WCA	0.08446	-9.1737	0.0930	0.00880	-0.02813
MSA	0.07858	-9.1393	0.1229	0.01449	-0.04864

TABLE III: Two-loop results for the critical temperature T_c, chemical potential ν_c, pressure P_c, density ρ_c, and energy u_c of the assymetric SPM. Various regularization schemes are considered, as explained in the text.

	T_c	ν_c	$10^2 \times \beta P_c$	ρ_c	$10 \times u_c$
OMF $\xi = 1$	0.1133	-7.8229	0.4181	0.0316	-0.1363
OMF $\xi = 2$	0.1263	-7.0281	0.5848	0.0336	-0.1209
OMF $\xi = 3$	0.1433	-6.1618	0.8049	0.0367	-0.0966
OMF $\xi = 4$	0.1585	-5.5175	1.0011	0.0396	-0.0691
OMF $\xi = 5$	0.1719	-5.0252	1.1744	0.0421	-0.0399
WCA $\xi = 1$	0.08428	-8.9142	0.1431	0.0137	-0.0461
WCA $\xi = 2$	0.09334	-8.2044	0.1903	0.0132	-0.0375
WCA $\xi = 3$	0.1058	-7.4035	0.2582	0.0137	-0.0305
WCA $\xi = 4$	0.1171	-6.8020	0.3208	0.0146	-0.0244
WCA $\xi = 5$	0.1272	-6.3422	0.3770	0.0155	-0.0183
MSA $\xi = 1$	0.07993	-9.0623	0.1379	0.0172	-0.0602
MSA $\xi = 2$	0.08422	-8.4828	0.1926	0.0199	-0.0628
MSA $\xi = 3$	0.09060	-7.7191	0.2751	0.0231	-0.0602
MSA $\xi = 4$	0.09677	-7.0701	0.3555	0.0257	-0.0527
MSA $\xi = 5$	0.1025	-6.5333	0.4302	0.0279	-0.0422

TABLE II: Two-loop results for the critical temperature T_c, chemical potential ν_c, pressure P_c, density ρ_c, and energy u_c of the RPM. Various regularization schemes are considered, as explained in the text.

	T_c	ν_c	$10^2 \times \beta P_c$	ρ_c	$10 \times u_c$
OMF	0.1133	-7.8229	0.4181	0.0316	-0.1363
WCA	0.08428	-8.9142	0.1431	0.0137	-0.0461
MSA	0.07993	-9.0623	0.1379	0.01722	-0.06021